2009

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Disciplines

Physical Sciences and Mathematics

Publication Details

Cox, B. J. & Hill, J. M. (2009). Polyhedral model for boron nitride nanotubes. In S. Hendy & I. Brown (Eds.), Advanced Materials and Nanotechnology: Proceedings of the International Conference (AMN-4). Volume 1151 (pp. 75-78). College Park, USA: American Institute of Physics.

Polyhedral model for boron nitride nanotubes

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Abstract. The conventional rolled-up model for nanotubes does not apply to very small radii tubes, for which curvature effects become significant. An existing geometric model for carbon nanotubes proposed by the authors, which accommodates this deficiency and which is based on the exact polyhedral cylindrical structure, is extended to a nanotube structure involving two species of atoms in equal proportion, and in particular boron nitride nanotubes. This generalisation allows the principle features to be included as the fundamental assumptions of the model, such as equal bond length but distinct bond angles and radii between the two species. The polyhedral model is based on the five simple geometric assumptions: (i) all bonds are of equal length; (ii) all bond angles for the boron atoms are equal; (iii) all boron atoms lie at an equal distance from the nanotube axis; (iv) all nitrogen atoms lie at an equal distance from the nanotube axis; and (v) there exists a fixed ratio of pyramidal height τ, between the boron species compared with the corresponding height in a symmetric single species nanotube. Working from these postulates, expressions are derived for the various structural parameters such as radii and bond angles for the two species for general values of the chiral vector numbers (n,m). The new model incorporates the additional constant of proportionality τ, which we assume applies to all nanotubes comprising the same elements and is such that $\tau = 1$ for a single species nanotube. Comparison with *ab initio* studies suggest that this assumption is entirely reasonable, and in particular we determine the value $\tau = 0.56 \pm 0.04$ for boron nitride.

Keywords: Boron nitride nanotubes, Nanostructures, Modelling, Polyhedra
PACS: 61.46.Np, 61.50.Ah

INTRODUCTION

The conventional theoretical model for carbon nanotube structure is that proposed by Dresselhaus et al. [1], in which all carbon atoms and bonds are assumed to be equal and lie in a flat plane that is subsequently rolled into a right circular cylinder to form the nanotube. One shortcoming of this model is that while all angles and all bonds begin equivalent to one another, after the process of rolling the plane into a cylinder, curvature effects will be apparent for some bonds and some angles more than others, depending on their orientation relative to the chiral vector. The present authors have proposed a new model for carbon nanotubes [2] which is based on a polyhedral structure that ensures all the bond lengths and bond angles are equal in the nanotube in the three dimensional state. Therefore, the unwanted curvature effects of rolling the nanotube into a cylinder are avoided and this new model is demonstrated to be in excellent agreement with *ab initio* calculations. The polyhedral model has also been employed to model ultra-small carbon nanotubes [3] (such as those which may be grown in zeolite channels) and the model is shown to predict novel and counterintuitive structures in the limit of very small radii nanotubes. Polyhedral models have also been proposed for other single chemical species nanotubes, such as silicon [4] and boron [5].

As shown in Figure 1, the polyhedral model is based on a correct three dimensional polyhedron where every vertex represents the position of an atomic nucleus and edges which join nearest neighbour atoms represent covalent bonds. The polyhedron for a nanotube is constructed by constructing a polyhedron comprising entirely equilateral triangles such that every vertex in the structure is equidistant from the cylindrical axis. At this point in the construction the vertices represent atoms from one of the triangular sublattices and the edges join atoms in the same sublattice and therefore only represent next-nearest neighbour relationships in the graphene structure and not covalent bonds. The next step in the

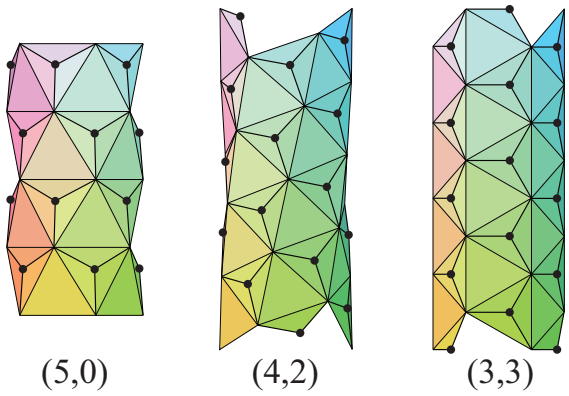


FIGURE 1. Three example boron nitride nanotubes represented as polyhedra, with a $\tau = 0.56$ and (n,m) as shown. (Boron atoms marked • and nitrogen atoms unmarked.)

CP1151, *Advanced Materials and Nanotechnology,* edited by Shaun C. Hendy and Ian W. M. Brown

construction is to position a right triangular pyramid on every second triangle. The pyramid bases match exactly the equilateral triangles and thus the three base vertices represent atoms from the first triangular sublattice and the apices of the pyramids represent the atoms from the second sublattice. The slant edges of the pyramids represent the covalent bonds between adjacent atoms in the graphene structure. The height of the pyramid is determined so that all the vertices of the pyramid (base vertices and apex) are equidistant from the same cylindrical axis. In this way, a perfectly symmetrical structure is produced with all bond lengths and all bond angles are equal and all atoms lie the same perpendicular distance from a common axis.

In the following section we outline how the polyhedral model for a single species nanotube may be modified for a two species nanotube. Following that we compare the results of the model applied to boron nitride nanotubes with numerical models from the literature and finally we discuss the results and state some conclusions.

TWO SPECIES POLYHEDRAL MODEL

The model described here can be applied to any two species chemical compound nanotube which forms a hexagonal lattice with alternating elements, such that each of the two triangular sublattices comprise entirely of one chemical species or the other. However, for the purposes of the remainder of this paper we will discuss specifically boron nitride nanotubes.

The essential feature that we wish to encapsulate in our model is the distinct radii which are seen for boron nitride nanotubes. Several researchers [6, 7, 8] find that the boron atoms all lie one distance from the nanotube axis r_B and the nitrogen atoms lie another slightly larger distance r_N from the same axis. The element specific structure is also apparent in the bond angles and Barnard et al. [7] who find that boron has bonds in a more planar arrangement close to 120°, whereas nitrogen has bonds that are bent more out of the plane and the adjacent bond angles vary from 120° more than is seen for boron. In order to model these features we propose a polyhedral model for boron nitride which is based on the five postulates:

(i) all bonds are of equal length σ;

(ii) all bond angles for the boron atoms are equal to ϕ_B;

(iii) all boron atoms lie at an equal distance from the nanotube axis r_B;

(iv) all nitrogen atoms lie at an equal distance from the nanotube axis r_N; and

(v) there exists a fixed ratio of pyramidal height τ, between the boron species compared with the corresponding height in a symmetric single species nanotube.

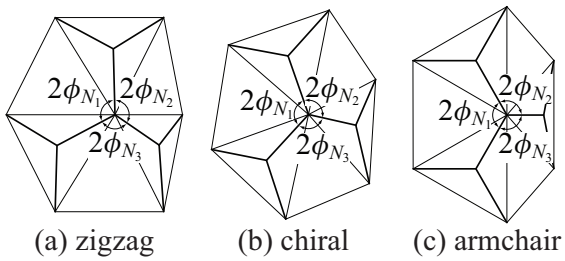
The key postulate to the development of this polyhedral model is (v) which cannot be physically motivated but we note that a linear relationship between the pyramidal height in the one species and two species models is the simplest assumption that can be made and so should be tested first. We note that a linear relationship also has the desirable and necessary feature of being invariant under stretching transformations. This means that we obtain the same numerical value of τ irrespective of the units of length which might be employed. We would certainly expect any reasonable physical hypothesis to enjoy this feature. The ratio τ may be thought of as a measure of the proportion of the energy associated with deforming the bonds at a boron site as compared to the corresponding energy for deforming the bonds at a nitrogen site. Finally, we note that while we postulate that a wide range of boron nitride nanotubes are characterized by the same value of τ we would expect that this value is specific to boron nitride and that other two species chemical compounds would be characterized by a different value of τ.

From these postulates and following a similar approach to that contained in [2] the authors produce analytical expressions for all the major geometrical parameters of boron nitride nanotubes in [9]. However, the construction does depend on finding the root of a transcendental equation which cannot be written explicitly and thus rather than just providing the analytical expressions we also undertake asymptotic expansions of the analytical expressions and we give the terms to the leading two orders of the expansion, which we will present here. The radii of the nanotubes are given by

$$r_B \approx \frac{\sigma\sqrt{3\Delta}}{2\pi} + \frac{\sqrt{3}\sigma\pi\left[4\Delta^3 - 9n^2m^2(n+m)^2\right]}{64\Delta^{7/2}} - \frac{\sqrt{3}\sigma\pi(7-\tau)(1-\tau)}{48\Delta^{1/2}}, \quad (1)$$

$$r_N \approx \frac{\sigma\sqrt{3\Delta}}{2\pi} + \frac{\sqrt{3}\sigma\pi\left[4\Delta^3 - 9n^2m^2(n+m)^2\right]}{64\Delta^{7/2}} + \frac{\sqrt{3}\sigma\pi(1-\tau^2)}{48\Delta^{1/2}}, \quad (2)$$

where (n,m) are the chiral vector numbers, $\Delta = n^2 + nm + m^2$, and σ is the boron-nitrogen bond length. We comment that the first term in both expressions is precisely the conventional rolled-up radius for a carbon nanotube, the second term in both formulae is the correction term found in the polyhedral model for a single species nanotube, and the third terms are the τ specific leading order expressions which distinguish the boron radius from the nitrogen radius.



(a) zigzag (b) chiral (c) armchair

FIGURE 2. Details of the zigzag, chiral and armchair nanotubes showing the bond angles (assuming a vertical nanotube axis).

From postulate (ii), all the boron bond angles ϕ_B are assumed to be equal. However, the nitrogen bond angles are assumed to be distinct and denoted by ϕ_{N_i}, where $i \in \{1,2,3\}$, as shown in Figure 2. The the two leading order terms of the boron bond angle (in degrees) are given by

$$2\phi_B^\circ \approx 120 - \frac{15\sqrt{3}\pi\tau^2}{\Delta}, \tag{3}$$

where the first term is angle in the hexagonal plane and the second term is the leading order curvature correction as found in the single species polyhedral model scaled by τ^2. The nitrogen bond angles ϕ_{N_i} are given by

$$2\phi_{N_1}^\circ \approx 2\phi_B - \frac{30\sqrt{3}\pi(1-\tau)(n-m)^2}{\Delta^2}, \tag{4}$$

$$2\phi_{N_2}^\circ \approx 2\phi_B - \frac{30\sqrt{3}\pi(1-\tau)(n+2m)^2}{\Delta^2}, \tag{5}$$

$$2\phi_{N_3}^\circ \approx 2\phi_B - \frac{30\sqrt{3}\pi(1-\tau)(2n+m)^2}{\Delta^2}, \tag{6}$$

which show that the additional terms for the nitrogen bond angle depends on $1-\tau$, so that when $\tau = 1$ then all the bond angles are equivalent.

Finally we present a formula which can be used to give a simple approximate value of the constant of proportionality τ if the boron and nitrogen radii and the bond length are known,

$$\tau \approx 1 - \frac{(r_N - r_B)(r_N + r_B)^2}{\sigma^2 r_N}. \tag{7}$$

However, we comment that there are more accurate methods for determining the ratio τ as described in [9] which are used in the next section to compare the results of the model with *ab initio* studies from the literature.

RESULTS

We begin by examining the results of Akdim et al. [6] who examine boron nitride nanotubes using a full potential linear combination of atomic orbitals approach. They report boron and nitrogen radii for a number of zigzag and armchair nanotubes. In Table 1 we show that the computed value of the bond length is in excellent agreement with the values measured in that study and a consistent value of the ratio τ is computed which lies in a range from approximately 0.58 to 0.60 for a number of nanotubes a with a range of radii and chirality.

TABLE 1. Results of Akdim et al. [6] (their values are indicated with an asterisk).

Nanotube	$\sigma^\star$ [Å]	$r_B^\star$ [Å]	$r_N^\star$ [Å]	τ	σ [Å]
(6,0)	1.446	2.393	2.485	0.59	1.441
(8,0)	1.443	3.185	3.254	0.58	1.441
(6,6)	1.441	4.125	4.177	0.59	1.443
(9,9)	1.440	6.188	6.222	0.60	1.441
(10,10)	1.438	6.857	6.888	0.60	1.438

TABLE 2. Results of Baumeier et al. [8] (their values are indicated with an asterisk).

Nanotube	$r_B^\star$ [Å]	$r_N^\star$ [Å]	τ	σ [Å]
(4,0)	1.526	1.675	0.54	1.380
(5,0)	1.918	2.040	0.53	1.392
(6,0)	2.314	2.415	0.53	1.399
(7,0)	2.715	2.800	0.54	1.406
(8,0)	3.112	3.185	0.55	1.410
(9,0)	3.511	3.575	0.56	1.414
(10,0)	3.938	3.995	0.56	1.427
(15,0)	5.888	5.925	0.57	1.423
(4,4)	2.656	2.745	0.52	1.404
(5,5)	3.367	3.435	0.54	1.417
(6,6)	4.060	4.115	0.56	1.422
(7,7)	4.749	4.795	0.57	1.424
(8,8)	5.435	5.475	0.57	1.425
(9,9)	6.119	6.155	0.57	1.426
(10,10)	6.803	6.835	0.57	1.426
(15,15)	10.218	10.240	0.56	1.427

In Table 2 we compare our results with those of Baumeier et al. [8] who investigate a large number of boron nanotubes using density functional theory and employing self-interaction-corrected pseudopotentials. Again Baumeier et al. [8] report the nanotube radii and by employing a precise method to determine the values of τ and σ we find that our results produce a value of the bond length σ which approaches the value of 1.43 Å, which is the value that Baumeier et al. [8] report for flat boron nitride. The value computed for the ratio τ is slightly smaller that that found in the previous study but it is still close and there is considerable consistency within this study with τ varying from approximately 0.52 to 0.57.

Finally we compare our model with the results of Barnard et al. [7] as shown in Table 3. Barnard et al. [7] employ density function theory within the generalised-gradient approximation, and they report the average

TABLE 3. Results of Barnard et al. [7] (their values are indicated with an asterisk).

Nanotube	$2\phi_N^\star$ [°]	τ	$2\overline{\phi}_N$ [°]
(6,6)	118.48 ± 0.82	0.57	118.49 ± 0.89
(9,9)	119.32 ± 0.38	0.57	119.32 ± 0.40
(12,12)	119.62 ± 0.21	0.56	119.61 ± 0.23

and deviation of bond angles in the nanotube structure. Therefore our method is to use the boron angles they report to compute a value for τ, and then compare the nitrogen bond angles we predict ϕ_{N_i} with the mean and deviation reported in the numerical study. From Table 3, we see that the value of τ is a reasonably consistent value ranging from 0.56 to 0.57. More strikingly, however, is the comparison of nitrogen bond angles where both the mean value and the variation show excellent agreement with the numerical study. Unfortunately, Barnard et al. [7] only consider three different boron nitride nanotubes of the type considered here and all three were of the armchair type $(n = m)$.

It may be seen from symmetry that for the armchair and zigzag nanotubes that two of the nitrogen bond angles are equal. Specifically, for armchair nanotubes $\phi_{N_2} = \phi_{N_3}$, and for zigzag nanotubes $\phi_{N_1} = \phi_{N_2}$. Finally, we note that in the case of armchair nanotubes $n = m$, the boron bond angle is precisely equal to the first nitrogen bond angle (that is, $\phi_B = \phi_{N_1}$) and this result is independent of the choice of τ and σ. This can be shown to be necessary for armchair nanotubes because in this case there must exist chains of alternating boron and nitrogen atoms for which all atoms of each species lie on lines which are parallel to each other and also to the nanotube axis, and these atoms are also bonded directly to one another, forming an alternating zigzag pattern between the two parallel lines. Since the lines are parallel and all bonds are of equal length, it follows that the boron-nitrogen-boron triangles are congruent to the nitrogen-boron-nitrogen triangles and therefore $\phi_B = \phi_{N_1}$.

CONCLUSION

In this paper we present a polyhedral geometric model for two species nanotubes which can be used to predict the species distinct radii and bond angles which are found in these nanostructures. The model is based on four symmetry postulates and a fifth postulate which assumes that the pyramidal height in the model can be related to the equivalent height in a single species structure via a linear constant ratio of proportionality τ. Comparison with three numerical studies show that there is reason to believe that the value of τ is reasonably constant over a range of nanotubes of differing sizes and chirality. Therefore as a first approximation we propose that the model is useful but as a refinement perhaps the value of τ could in fact be a function of the chiral vector numbers (n,m). Finally we note that while this model is applicable to any two species nanotube with a hexagonal lattice, we would expect that the value of τ is not fixed for all chemical species. That is, the value of $\tau \approx 0.56$ determined here is thought to be specific to boron nitride and any other two species materials would exhibit another value of τ.

ACKNOWLEDGMENTS

The support of the Australian Research Council, both through the Discovery Project Scheme and for providing an Australian Professorial Fellowship for JMH and an Australian Postdoctoral Fellowship for BJC is gratefully acknowledged.

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